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(71) Applicant: ESSEX SPECIALTY PRODUCTS, INC. [US/US]; 1250 Harmon Road, Auburn Hills, MI 48326 (US).

(72) Inventors: HSIEH, Harry, W.; 1696 Picadilly Drive, Troy, MI 48084 (US). MAHDI, Syed, Z.; Apartment 219, 262 Woodside Court, Rochester Hills, MI 48307 (US).

(74) Agent: SIMS, Norman, L.; Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).

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(54) Title: POLYURETHANE SEALANT COMPOSITIONS

(57) Abstract

In one aspect, this invention is a polyurethane sealant composition comprising: (1) a urethane prepolymer having an isocyanate-functionality of at least 2.0 and a weight average molecular weight of at least 2,000; and (2) a catalytic amount of (a) a substantially active hydrogen-free glycol acid salt of a tertiary amine and an organometallic compound, (b) a mixture of a substantially active hydrogen-free glycol acid salt of a tertiary amine and a second organometallic compound, or (c) a mixture of an organotin compound with dimorpholinodialkyl ether or a dialkylmorpholinodialkyl ether, or (d) a mixture of a substantially active hydrogen-free glycol acid salt of a tertiary amine and an organometallic compound, a second organometallic compound and dimorpholinodialkyl ether or di((dialkylmorpholino)alkyl)ether. In another embodiment, the polyurethane sealant composition further comprises (A) a silane, or (B) an adduct of an isocyanate-reactive silane and a polyisocyanate, (C) the reaction product of an isocyanate-reactive silane or an adduct of an isocyanate-reactive silane and a polyisocyanate with a polyisocyanate and an active hydrogen-containing compound or a polyurethane prepolymer which has free isocyanate moieties; which reaction product has an average of at least one silane group and at least one isocyanate group per molecule. In another embodiment, the invention is a method for bonding glass to a substrate which comprises contacting a sealant according to the invention with glass and another substrate with the sealant disposed between the glass and substrate, and thereafter allowing the sealant to cure so as to bind the glass to the substrate. The sealant composition of the invention is useful in bonding glass substrates to metal, plastic, fiberglass or composite substrates, which may or may not be painted. It has been discovered to give unexpectedly high lap shear strength when no primer compositions have previously been applied to the painted plastic, metal, fiberglass or composite substrate.

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POLYURETHANE SEALANT COMPOSITIONS

This invention relates to polyurethane sealant compositions which are capable of being used without the need for a primer.

Polyurethane sealant compositions typically comprise at least one urethane prepolymer. Sealants useful for bonding to non-porous substrates, such as glass are described, for example, in U.S. Patent 4,374,237 and U.S. Patent 4,687,533. U.S. Patent 4,374,237 describes a polyurethane sealant containing urethane prepolymers which have been further reacted with secondary amine compounds containing two silane groups. U.S. Patent 4,687,533 describes a polyurethane sealant containing urethane prepolymers which contain silane groups which have been prepared by reacting a polyisocyanate having at least three isocyanate groups with less than an equivalent amount of an alkoxysilane having a terminal group containing active hydrogen atoms reactive with isocyanate groups to form an isocyanatosilane having at least two unreacted isocyanate groups. In a second step, the isocyanatosilane is mixed with additional polyisocyanate and the mixture is reacted with a polyol to form a polyurethane prepolymer having terminal isocyanato groups and pendant alkoxysilane groups.

However, when such sealants are used to bond glass substrates to painted substrates, such as for window installation in vehicle manufacturing, the lap shear strength of the bonded substrate may be less than desirable for safety or structural purposes. Consequently, a separate paint primer comprising a solution of one or more silanes is typically applied to a painted substrate prior to the application of the sealant in most vehicle assembly operations for bonding the windshield and the rear window. The use of a primer in assembly operations is undesirable in that it introduces an extra step, additional cost, the risk of marring the paint surface if dripped on an undesired location and exposes the assembly line operators to additional chemicals. It would be desirable to provide a polyurethane sealant which, when bonded to a painted substrate and cured, provides a bonded substrate with a higher lap shear strength, particularly when used in the absence of a paint primer.

In one aspect, this invention is a polyurethane sealant composition comprising (1) a urethane prepolymer having an isocyanate-functionality of at least 2.0 and a weight average molecular weight of at least 2,000; and (2) a catalytic amount of (a) a substantially active hydrogen-free glycol acid salt of a tertiary amine and an organometallic compound, (b)

a mixture of a substantially active hydrogen-free glycol acid salt of a tertiary amine and an organometallic compound and a second organometallic compound, or (c) a mixture of an organotin compound with dimorpholinodialkyl ether or a di((dialkylmorpholino)alkyl) ether; or (d) a mixture of a substantially active hydrogen-free glycol acid salt of a tertiary amine and an organometallic compound, a second organometallic compound and dimorpholinodialkyl ether or di((dialkylmorpholino)alkyl) ether.

In another embodiment, the polyurethane sealant composition further comprises (A) a silane, or (B) an adduct of an isocyanate-reactive silane and a polyisocyanate, (C) the reaction product of (1) (a) an isocyanate-reactive silane or (b) an adduct of an isocyanate-reactive silane and a polyisocyanate with (2) (a) a polyisocyanate and an active hydrogen-containing compound or (b) a polyurethane prepolymer which has free isocyanate moieties; which reaction product has an average of at least one silane group and at least one isocyanate group per molecule.

In another embodiment the invention is a method for bonding glass to a substrate which comprises contacting a sealant according to the invention with glass and another substrate with the sealant disposed between the glass and substrate and thereafter allowing the sealant to cure so as to bind the glass to the substrate.

The sealant composition of the invention is useful in bonding glass substrates to plastic, metal, fiberglass and composite substrates which may or may not be painted. It has been discovered to give unexpectedly high lap shear strength when no primer compositions have previously been applied to a painted plastic, metal, fiberglass or composite substrate.

Suitable urethane prepolymers for use in preparing the composition of the invention include any compound having an average isocyanate-functionality of at least 2.0 and a molecular weight of at least 2,000. Preferably, the average isocyanate- functionality of the prepolymer is at least 2.2, and is more preferably at least 2.4. Preferably the isocyanate-functionality is no greater than 4.0, more preferably, no greater than 3.5 and most preferably, no greater than 3.0. Preferably, the weight average molecular weight of the prepolymer is at least 2,500, and is more preferably at least 3,000; and is preferably no greater than 40,000, even more preferably, no greater than 20,000, more preferably, no greater than 15,000, and is most preferably, no greater than 10,000. The prepolymer may be prepared by any suitable method, such as by reacting an isocyanate-reactive compound containing at least

two isocyanate-reactive groups with an excess over stoichiometry of a polyisocyanate under reaction conditions sufficient to form the corresponding prepolymer.

Suitable polyisocyanates for use in preparing the prepolymer include any aliphatic, cycloaliphatic, araliphatic, heterocyclic or aromatic polyisocyanate, or mixture thereof. Preferably the polyisocyanates used have an average isocyanate- functionality of at least 2.0 and an equivalent weight of at least 80. Preferably, the isocyanate-functionality of the polyisocyanate is at least 2.0, more preferably at least 2.2, and is most preferably at least 2.4; and is preferably no greater than 4.0, more preferably no greater than 3.5, and is most preferably no greater than 3.0. Higher functionalities may also be used, but may cause excessive cross-linking, and result in an adhesive which is too viscous to handle and apply easily, and can cause the cured adhesive to be too brittle. Preferably, the equivalent weight of the polyisocyanate is at least 100, more preferably at least 110, and is most preferably at least 120; and is preferably no greater than 300, more preferably no greater than 250, and is most preferably no greater than 200. Preferably the isocyanate used is an aromatic isocyanate. More preferably the isocyanate is diphenyl methane diisocyanate. Examples of useful polyisocyanates are disclosed in U.S. Patent 5,672,652 at column 3 line 5 to line 51.

Preferred polyisocyanates include diphenylmethane-4,4'-diisocyanate and polymeric derivatives thereof, isophorone diisocyanate, tetramethylxylene diisocyanate, 1,6-hexamethylene diisocyante and polymeric derivatives thereof, bis(4-isocyanatocylohexyl)methane, and trimethyl hexamethylene diisocyanate.

The term "isocyanate-reactive compound" as used herein includes any organic compound having at least two isocyanate-reactive moieties, such as a compound containing an active hydrogen moiety, or an imino-functional compound. For the purposes of this invention, an active hydrogen-containing moiety refers to a moiety containing a hydrogen atom which, because of its position in the molecule, displays significant activity according to the Zerewitnoff test described by Wohler in the Journal of the American Chemical Society, Vol. 49, p. 3181 (1927). Illustrative of such active hydrogen moieties are -COOH, -OH, $-NH_2$, -NH-, $-CONH_2$, -SH, and -CONH-. Preferable active hydrogen-containing compounds include polyols, polyamines, polymercaptans and polyacids. Suitable imino-functional compounds are those which have at least one terminal imino group per molecule, such as are described, for example, in U.S. Patent 4,910,279. Preferably, the isocyanate--reactive compound is a polyol, and is more preferably a polyether polyol. Examples of

polyols useful in preparing the prepolymers are disclosed in U.S. Patent 5,672,652 at column 4 line 5 to line 60.

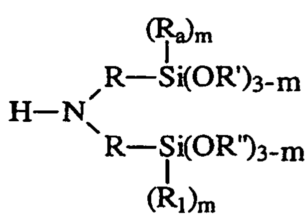
Preferably, the isocyanate-reactive compound has a functionality of at least 1.5, more preferably at least 1.8, and is most preferably at least 2.0; and is preferably no greater than 4.0, more preferably no greater than 3.5, and is most preferably no greater than 3.0. Preferably, the equivalent weight of the isocyanate-reactive compound is at least 200, more preferably at least 500, and is more preferably at least 1,000; and is preferably no greater than 5,000, more preferably no greater than 3,000, and is most preferably no greater than 2,500.

The prepolymer may be prepared by any suitable method, such as bulk polymerization and solution polymerization. See U.S. Patent 5,672,652, column 5 line 5 to line 15. The isocyanate content in the prepolymers is preferably in the range of 0.1 percent to 10 percent, more preferably in the range of 1.5 percent to 5.0 percent and most preferably in the range of 1.8 percent to 3.0 percent.

The prepolymer is present in the sealant composition in sufficient amount such that the sealant is capable of bonding glass to metal, plastic, fiberglass or composite substrates, preferably the substrates are painted and more preferably the substrates are painted with acid resistant paints. More preferably the polyurethane prepolymer is present in an amount of 30 percent by weight or greater based on the weight of the sealant, even more preferably 50 percent by weight or greater and most preferably 70 percent by weight or greater. More preferably the polyurethane prepolymer is present in an amount of 99.8 percent by weight or less based on the weight of the sealant and most preferably 85 percent by weight or less.

In those embodiments where the sealant is used to bond glass to substrates coated with acid resistant paints it is desirable to have a silane present in some form. The silane may be blended with the prepolymer. In another embodiment the silane is a silane which has an active hydrogen atom which is reactive with an isocyanate. Preferably such silane is a mercapto-silane or an amino-silane and more preferably is a mercapto-trialkoxy-silane or an amino-trialkoxy silane. In one embodiment, the silane having, an active hydrogen atom reactive with isocyanate moieties, can be reacted with the terminal isocyanate moieties of the prepolymer. Such reaction products are disclosed in U.S. Patent 4,374,237 and 4,345,053. In yet another embodiment, the silane having a reactive hydrogen

moiety reactive with an isocyanate moiety can be reacted into the backbone of the prepolymer by reacting such silane with the starting materials during the preparation of the prepolymer. The process for the preparation of prepolymers containing silane in the backbone is disclosed in U.S. Patent 4,625,012. Such silane, having active hydrogen moieties, can be reacted with a polyisocyanate to form an adduct which is blended with the prepolymer reacted with a polyurethane prepolymer or reacted with a polyisocyanate and a compound having on average more than one moiety reactive with an isocyanate moiety. Preferably the adduct is a reaction product of a secondary amino- or mercapto-alkoxy silane and a polyisocyanate, the adduct having an average of at least one silane group and at least one isocyanate group per molecule (hereinafter "adduct"). Preferably the adduct has at least 1.5 isocyanate groups and at least one silane group per molecule, and most preferably has at least two isocyanate groups and at least one silane group per molecule. The adduct level in the sealant compositions is preferably in the range of 0.5 percent to 20 percent, more preferably in the range of 1.0 percent to 10 percent and most preferably in the range of 2.0 percent to 7 percent. The adduct may be prepared by any suitable method, such as, for example, by reacting a secondary amino- or mercapto-alkoxy silane with a polyisocyanate compound. Suitable polyisocyanates for use in preparing the adduct include those described above as suitable for use in preparing the prepolymer, particularly including isopherone diisocyanate, polymethylene polyphenylisocyanates, and aliphatic polyisocyanate such as hexamethylene diisocyanate. Preferably, the polyisocyanate is an aliphatic polyisocyanate and is most preferably an aliphatic polyisocyanate based on hexamethylene diisocyanate with an equivalent weight of 195. The polyisocyanate used to prepare the isocyanate silane adduct preferably has a molecular weight of 2,000 or less, more preferably 1,000 or less. Suitable organo-functional silanes include amino- or mercapto-alkoxysilanes of the formula:



$$HS—R—Si(R_1)_m(OR')_{(3-m)}$$

wherein R is a divalent organic group, preferably C_{1-4} alkylene, R', R'', R_1 and R_a are hydrogen or alkyl, preferably C_{1-4} alkyl, m is an integer from 0 to 2. Examples of such compounds are disclosed in U.S. Patent 5,623,044, column 5 line 21 to line 30. Preferably the organo-functional silane is gamma-mercaptopropyl-trimethoxysilane (available as A189

from Union Carbide) or N,N'-bis((3-trimethoxysilyl)propyl)amine. The adduct can be prepared as disclosed in U.S. Patent 5,623,044 column 5 line 44 to line 56.

The reactions to prepare the prepolymer and the adduct may be carried out in the presence of urethane catalysts as disclosed in U.S. Patent 5,623,044 at column 6 line 3 to line12.

In one embodiment the sealant composition of the invention further comprises a catalyst composition an active hydrogen free glycol acid salt of a tertiary amine and an organometallic compound. The tertiary amine is any tertiary amine which complexes with an organometallic compound and preferably has a pH of 8 to 12, and most preferably has a pH of 8 to 10. Preferred tertiary amines include triethylene diamine and 1,8-diazabicyclo[5,4,0]undecene. The organometallic compound can be any organometallic compound which is known as a catalyst in polyurethane reactions. Preferred organometallic compounds include dialkyltin dicarboxylates, such as 1,1-dibutyltin diacetate and 1,1-dimethyltin dilaurate. A preferred catalyst is an active hydrogen free glycol salt of triethylenediamine and 1,1-dibutyltin diacetate. The glycol salt of triethylenediamine and 1,1-dibutyltin diacetate is available from Air Products as DABCO DC2 catalyst. The glycol salt is modified by reacting it with a compound which reacts with active hydrogen atoms to neutralize them, preferably a polyisocyanate. Preferably the isocyanate is aliphatic and more preferably is nonsymmetric. Preferably the polyisocyanate and the salt are reacted in a solvent and plasticizer and in stoichiometric amounts, although an excess of the isocyanate may be used. Useful solvents include aromatic hydrocarbons, such as toluene and xylene. Plasticizers as disclosed herein may be used. Upon contacting the dissolved salt with the isocyanate the mixture exotherms. It may be exposed to heat for a period of time, and temperatures up to 100°C may be used. Preferably a temperature of 60°C to 85°C is used. The mixture is reacted until the active hydrogen atoms have been substantially removed. Substantially removed means all but a trace amount of the active hydrogen atoms have been removed. The catalyst composition may be used in an amount of 0.05 percent by weight or greater based on the weight of the sealant and preferably 0.2 percent by weight or greater. The catalyst may preferably be used in an amount of 4.0 percent by weight or less, based on the weight of the sealant, more preferably 1.0 percent by weight and most preferably 0.4 percent by weight or less.

The sealant composition of the invention also preferably contains one or more additional catalysts which have good stability in the absence of atmospheric moisture, but

which has a rapid cure rate in the presence of atmospheric moisture, such as an organometallic (preferably tin) catalyst, a dimorpholinodialkyl ether, a di((dialkylmorpholino)alkyl) ether or a mixture thereof. A preferred dimorpholinodialkyl ether is dimorpholinodiethyl ether. A preferred di((dialkylmorpholino)alkyl) ether is (di-(2-(3,5-dimethylmorpholino)ethyl)ether). The dimorpholinodialkyl ether or di((dialkylmorpholino)alkyl) ether when employed, are preferably employed in an amount, based on the weight of the sealant, of 0.01 percent by weight or greater based on the sealant, more preferably 0.05 percent by weight or greater, even more preferably 0.1 percent by weight or greater and most preferably 0.2 percent by weight or greater and 2.0 percent by weight or less, more preferably 1.75 percent by weight or less, even more preferably 1.0 percent by weight or less and most preferably 0.4 percent by weight or less. The organotin catalyst is preferably a dialkyltin dicarboxylate or a dialkyltin dimercaptide. The dialkyltin dicarboxylate preferably corresponds to the formula $(R^2OC(O))_2$-Sn-$(R^3)_2$ wherein R^2 and R^3 are independently in each occurrence a C_{1-10} alkyl, preferably a C_{1-3} alkyl and most preferably a methyl. Dialkyltin dicarboxylates with lower total carbon atoms are preferred as they are more active catalysts in the compositions of the invention. The preferred dialkyl dicarboxylates include 1,1-dimethyltin dilaurate, 1,1-dibutyltin diacetate and 1,1-dimethyl dimaleate. The organotin catalyst is present in an amount of 5 parts per million or greater, more preferably 60 parts per million or greater based on the weight of the sealant, most preferably 120 parts by million or greater. The organotin catalyst is preferably present in an amount of 1.0 percent or less based on the weight of the sealant, more preferably 0.5 percent by weight or less and most preferably 0.1 percent by weight or less.

In another embodiment of the invention the catalyst is a mixture of an organotin compound and a dimorpholinodialkyl ether or a di((dialkylmorpholino)alkyl) ether. Preferably the organotin compound is a dialkyltin dicarboxylate.

For formulating sealant compositions, the prepolymer and the adduct, if present, are combined, preferably with fillers and additives known in the prior art for use in elastomeric compositions. By the addition of such materials, physical properties such as viscosity, flow rate, and sag, can be modified. However, to prevent premature hydrolysis of the moisture sensitive groups of the polymer, the filler should be thoroughly dried before admixture therewith. Exemplary filler materials and additives include materials such as carbon black, titanium dioxide, clays, calcium carbonate, surface treated silicas, ultraviolet stabilizers, and antioxidants. This list, however, is not comprehensive and is given merely as

illustrative. The fillers are preferably present in an amount of 15 percent by weight or greater based on the amount of the sealant. The fillers are preferably present in an amount of 70 percent by weight or less based on the sealant, more preferably 50 percent by weight or less and even more preferably 30 percent by weight or less.

The amount of silane present is that amount which enhances the adhesion of the adhesive to the painted surface without the need for a primer. The amount of silane is preferably, 0.1 percent by weight or greater based on the weight of the sealant and most preferably, 1.0 percent by weight or greater. The amount of silane used is preferably, 10 percent by weight or greater or less and most preferably, 2.0 percent by weight or less.

The sealant composition also preferably contains one or more plasticizers or solvents to modify rheological properties to a desired consistency. Such materials should be free of water, inert to isocyanate groups, and compatible with the polymer. Such material may be added to the reaction mixtures for preparing the prepolymer or the adduct, or to the mixture for preparing the final sealant composition, but is preferably added to the reaction mixtures for preparing the prepolymer and the adduct, so that such mixtures may be more easily mixed and handled. Suitable plasticizers and solvents are well-known in the art and include dioctyl phthalate, dibutyl phthalate, a partially hydrogenated terpene commercially available as "HB-40", trioctyl phosphate, epoxy plasticizers, toluene-sulfamide, chloroparaffins, adipic acid esters, castor oil, xylene, 1-methyl-2-pyrrolidinone and toluene. The amount of plasticizer used is that amount sufficient to give the desired rheological properties and disperse the components in the sealant composition. Preferably the plasticizer is present in an amount of 0 percent by weight or greater, more preferably 5 percent by weight or greater and most preferably 10 percent by weight or greater. The plasticizer is preferably present in an amount of 45 percent by weight or less and 40 percent by weight or less and most preferably 20 parts by weight or less.

The sealant composition of this invention may be formulated by blending the components together using means well-known in the art. Generally the components are blended in a suitable mixer. Such blending is preferably conducted in an inert atmosphere and atmospheric moisture to prevent premature reaction. It may be advantageous to add any plasticizers to the reaction mixture for preparing the isocyanate-containing prepolymer so that such mixture may be easily mixed and handled. Alternatively, the plasticizers can be added during blending of all the components. Once the sealant composition is formulated, it is packaged in a suitable container such that it is protected from atmospheric moisture.

Contact with atmospheric moisture could result in premature crosslinking of the polyurethane prepolymer-containing isocyanate groups.

The sealant composition of the invention is used to bond porous and nonporous substrates together. The sealant composition is applied to a substrate and the adhesive on the first substrate is thereafter contacted with a second substrate. Thereafter the adhesive is exposed to curing conditions. In a preferred embodiment one substrate is glass and the other substrate is a plastic, metal, fiberglass or composite substrate which may optionally be painted. This method is especially effective for substrates painted with an acid resistant paint. In preferred embodiments, the surfaces to which the adhesive is applied are cleaned prior to application, see for example U.S. Patents 4,525,511, 3,707,521 and 3,779,794. Generally the sealants of the invention are applied at ambient temperature in the presence of atmospheric moisture. Exposure to atmospheric moisture is sufficient to result in curing of the sealant. Curing may be further accelerated by applying heat to the curing sealant by means of convection heat, or microwave heating. Preferably the sealant of the invention is formulated to provide a working time of 6 minutes or greater more preferably 10 minutes or greater. Preferably the working time is 15 minutes or less and more preferably 12 minutes or less.

Molecular weights and functionality as described herein are determined according to the procedures disclosed in WO 97125360.

Example 1

A polyether polyurethane prepolymer was prepared by thoroughly mixing 386 grams of a polyoxypropylene diol having an average molecular weight of 2000 and 559 grams of polyoxypropylene triol having an average molecular weight of 4500, in a 2-liter resin kettle equipped with a mechanical agitator, a nitrogen inlet adapter and a thermometer. Under nitrogen purge, the mixture was heated to 50°C. 170 Grams of molten diphenylene methane 4,4'-diisocyanate were added to the mixture and the mixture thoroughly mixed. Then 0.1 gram of stannous octoate was introduced and the mixture was mixed for two hours. Finally, 484 grams of alkyl phthalate plasticizer and 16 grams of diethyl malonate were added to the mixture. The resulting prepolymer had an isocyanate content of 1.47 percent by weight.

Example 2

A silane adduct formed between a secondary amino bis-alkoxysilane and a polyisocyanate was prepared by charging and then thoroughly mixing 60 grams of alkyl phthalate plasticizer and 150 grams (0.263 mol) of Desmodur™ N-100 (a reaction product of three moles of hexamethylene diisocyanate with one mole of water, supplied by Bayer USA Inc.) in a reactor equipped with a mechanical agitator, a thermometer, and a nitrogen inlet tube. To the above mixture, 90 grams (0.263 mole) of N,N'-bis((3-trimethoxysilyl)propyl)amine (TMSPA) were added. The mixture was mixed for 30 minutes. The adduct mixture had an isocyanate content of 7.1 percent by weight.

Example 3

A polyurethane prepolymer containing pendant silane groups was prepared by copolymerizing a diisocyanate, a polyether diol, a polyether triol, and a silane adduct. 200 Grams of a polypropylene ether diol having an average molecular weight of 2000, 272 grams of a polypropylene ether triol having an average molecular weight of 4500 and 15 grams of alkyl phthalate plasticizer were mixed and heated to 50°C in a reaction kettle under nitrogen. 45 Grams of the silane adduct in Example 2, and 78 grams of molten diphenylene methane 4,4'-diisocyanate were added to the kettle and thoroughly mixed. To the above mixture, 0.03 gram of stannous octoate catalyst was added. Mixing was continued for two hours. 282 Grams of alkylphthalate and 9 grams of diethyl malonate were added and uniformly mixed. The prepolymer had an isocyanate content of 1.3 percent by weight.

Example 4

A commercially available catalyst containing glycol as a solvent was treated with a diisocyanate compound to react away glycol, by first dissolving 10.8 grams of DABCO DC-2 (delay-action, amine-based catalyst, supplied by Air Products and Chemicals, Inc.) in the mixture of 27.7 grams of toluene, 9.2 grams of N-ethyl toluene sulfonamide and 21.6 grams of diethyl malonate in a reactor equipped with a mechanical agitator, a thermometer, and a nitrogen inlet tube. And then 30.8 grams of Vestanat™ TMDI (trimethyl hexamethylene diisocyanate supplied by Huls America, Inc.) was added under agitation. After exotherm subsided, the mixture was heated at 80°C for 6 hours. The final mixture was a liquid of light orange color and had zero percent isocyanate content by NCO titration.

Example 5

A moisture curable sealant composition was prepared under anhydrous conditions by first degassing under agitation the mixture of 1089 grams of the prepolymer of Example 1, and 15 grams of N,N'-bis((3-trimethoxysilyl)propyl)amine in a planetary mixer for 30 minutes. At this point, all the aminosilane was fully reacted with some isocyanate groups on the prepolymer. Then, to the above mixture, 65 grams of Desmodur™ N-3300 (an aliphatic polyisocyanate resin based on hexamethylene diisocyanate, supplied by Bayer USA Inc.) was charged and mixed for 10 minutes. Subsequently, 450 grams of dried carbon black was added, and mixed for 25 minutes under the reduced pressure of 30 inches of mercury. Finally, 14 grams of modified DABCO DC-2 of Example 4, were added and mixed for 10 minutes under the reduced pressure. The compounded sealant was filled into sealant tubes.

The following are tests used for the prepared sealants:

Quick Knife Adhesion Test:

A 6.3 mm (width) by 6.3 mm (height) by 76.2 mm (length) size sealant bead is placed on 101.6 mm x 101.6 mm piece of an acid resistant paint panel and the assembly is cured for a specific time in the condition of 23°C and 50 percent relative humidity. The cured bead is cut with a razor blade through to the painted surface at a 45 degree angle while pulling back the end of the bead at a 180 degree angle. Notches are cut every 3 mm on the painted surface. The degree of adhesion is evaluated as adhesive failure (AF) and/or cohesive failure (CF). In case of adhesive failure, the cured bead can be separated from the painted surface, while in cohesive failure, separation occurs within the sealant bead as a result of cutting and pulling. The tested paint substrate can be used as supplied, or treated by wiping with isopropanol (IPA) or naphtha (NP). For the sealant of the invention, adhesion of a sealant develops sooner to the treated substrate than to the untreated one.

Lap Shear Test:

A sealant approximately 6.3 mm wide by 8 mm high is applied along the width of the glass and approximately 6 mm to 12 mm from the primed end. The paint substrate is immediately placed on the sealant and the sample is allowed to cure at the condition of the 23°C and 50 percent relative humidity for 5 days. The sample was then pulled at a rate of 1 inch/minute (2.5 cm/minute) with an Instron Tester.

Environmental Tests:

Short-term environmental tests include four weeks in the condition of 24°C, 50 percent R.H., four weeks in a 90°C oven, and ten days in 32°C water. Samples also are subjected to weatherability tests according to SAE J1960 and SAE J 1885.

Quick Adhesion test:

A 4 by 1/4 inch (10.1 by 0.6 cm) bead of sealant is extruded from a sealant tube on to a primed glass plate. A paint substrate is immediately placed on the top of the sealant bead. This assembly is allowed to cure at the 23°C and 50 percent relative humidity condition for a specific length of time and then the two substrates were separated by pulling in a plane perpendicular to the plane of the sealant bead at 10 inches per minute (25.4 cm per minute). The curing rate is recorded in pounds per square inch (kilopascals) at the elapsed time after assembly.

The stability of the sealant on storage is evaluated by determining the flow rates of a sealant before and after aging at 130°F (54°C) for three days. The press flow is determined as the time in seconds required to extrude 20 grams of the sealant through an orifice 0.157 inch (0.4 cm) in diameter under a pressure of 80 pounds per square inch (551 kPa). Percent growth in press flow after aging will indicate the stability of the sealant on storage.

The sealant in Example 5 had a very good accelerated storage stability as shown in press flows of 19 and 20 seconds respectively before and after aging at 130°F (54°C) for 3 days. The Quick Knife Adhesion test showed that the sealant adhered in one day to the IPA-wiped acid resistant paint and in 2 days to the untreated one. In lap shear testing, the sealant developed an average lap shear strength of 544 psi (3748 kPa) on both the treated and untreated paint substrates after 5 day cure at the condition of 23°C and 50 percent R.H. The cured sealant produced 168 psi (1157 kPa) of tear strength, and 1085 psi (7476 kPa) of tensile strength and 270 percent elongation at break. The cure rate by the Quick Adhesion test, for this sealant were: 4 psi (28 kPa) at 1.5 hour, 24 psi (165 kPa) at 3 hours and 84 psi (579 kPa) at 6 hours.

Example 6

This sealant has the same composition as sealant in Example 5 except that a combination of 6 grams of the modified catalyst in Example 4, and 5 grams of dimorpholinodiethyl ether (DMDEE) was used instead of 14 grams of the modified catalyst alone. The cured sealant has similar adhesion and physical properties as the sealant in Example 5. The cure rates by the Quick Adhesion test at the condition of 23°C and 50 percent R.H., for this sealant were: 23 psi (158 kPa) at 1.5 hour, 63 psi (434 kPa) at 3 hours and 100 psi (689 kPa) at 6 hours. When exposed to the SAE J 1960 condition, the cured lap shear samples prepared from this material using glass primer on the glass side and no paint primer on the IPA-wiped paint substrate, exhibited an average lap shear strength of 525 psi (3617 kPa), and 100 percent cohesive failure within the sealant after 2,000 hours of exposure.

Example 7

Additional moisture curable sealants were also prepared in the same fashion as described in Example 5. Their compositions and adhesion properties by Quick Knife Adhesion to acid resistant paint are tabulated below.

Table I

Ingredient (% by weight)	Ex-7	Ex-8	Ex-9	Ex-10	Ex-11	Ex-12
Prepolymer in Example 1	1021	1089	--	1089	1089	1021
Prepolymer in Example 3	--	--	1115	--	--	--
TMSPA	15	5	--	17	15	15
Silane Adduct in Example 2	55	--	--	--	--	55
Desmodur N-3300	--	13	45	68	--	64
PAPI 2020	--	35	--	--	--	--
Carbon Black	500	450	450	375	450	500
Calcium Carbonate	--	--	--	274	--	--
Catalyst in Example 4	18	35	6	7	6	6
Bismuth Octoate	--	--	--	--	--	--
Stannous Octoate	--	--	--	--	--	--
DMDEE	5	--	5	6	5	5
1-Methyl-2-pyrrolidinone	--	--	--	--	--	--
Alkyl Phthalate Plasticizer	10	--	--	--	--	--
Total	1624	1637	1621	1836	1565	1666
Days required to have adhesion to substrate with wipe	1	5	1	1	6	2
without wipe	2	5	2	1	> 10	4

Table II

Ingredient (% by weight)	Ex-13	Ex-14	Ex-15	Ex-16	Ex-17	Ex-18	Ex-19	Ex-20
Prepolymer in Example 1	1089	1089	1089	1089	1089	1089	1089	938
TMSPA	15	15	15	15	15	15	15	--
Silane Adduct in Example 2	--	--	--	--	--	--	--	165
Desmodur N-3300	71	71	71	71	71	65	65	--
Catalyst in Example 4	6	6	6	--	6	--	--	--
Bismuth Octoate	--	--	--	--	--	8	--	--
Stannous Octoate	--	--	--	--	--	--	2	--
DMDEE	3	5	5	5	5	--	--	5
1,1-Dimethyltin Dilaurate	--	--	--	0.2	0.2	--	--	--
Alkyl Phthalate Plasticizer	--	--	--	1.8	1.8	--	--	35
1,1-Dibutyltin Diacetate	2	--	--	--	--	--	--	--
1,1-Dimethyltin Mercaptide	--	--	2	--	--	--	--	--
1-Methyl-2-pyrrolidinone	--	--	--	--	--	20	20	--
Dimethyltin dimaleate	--	2	--	--	--	--	--	--
Carbon Black	493	493	493	493	493	450	450	500
Total	1679	1681	1681	1675	1681	1647	1641	1643
Days required to have adhesion to substrate with wipe without wipe	1 2	1 2	1 2	1 1	1 1	no adhesion	no adhesion	no adhesion

CLAIMS:

1. A sealant composition comprising (1) a urethane prepolymer having an isocyanate-functionality of at least 2.0 and a weight average molecular weight of at least 2,000; and (2) a catalytic amount of (a) a substantially active hydrogen-free glycol acid salt of a tertiary amine and an organometallic compound, (b) a mixture of a substantially active hydrogen-free glycol acid salt of a tertiary amine and an organometallic compound and a second organometallic compound, (c) a mixture of a dialkyltin dicarboxylate with dimorpholinodialkyl ether or a di((dialkylmorpholino)alkyl) ether or (d) a mixture of a substantially active hydrogen- free glycol acid salt of a tertiary amine and an organometallic compound, a second organometallic compound and dimorpholinodialkyl ether or di((dialkylmorpholino)alkyl) ether.

2. The sealant composition of Claim 1 which further comprises (A) a silane, or (B) an adduct of an isocyanate-reactive silane and a polyisocyanate, (C) the reaction product of (1) (a) an isocyanate-reactive silane or (b) an adduct of an isocyanate-reactive silane and a polyisocyanate with (2) (a) a polyisocyanate and an active hydrogen-containing compound or (b) a polyurethane prepolymer which has free isocyanate moieties which reaction product has an average of at least one silane group and at least one isocyanate group per molecule.

3. The sealant composition of Claims 1 or 2 wherein the substantially active hydrogen-free glycol acid salt of tertiary amine and the organometallic compound is the reaction product of a polyisocyanate and a glycol acid salt of tertiary amine and an organometallic compound.

4. The sealant composition of any one of Claims 1 to 3 wherein the tertiary amine has a pH of 8 to 10.

5. The sealant composition of any one of Claims 1 to 4 wherein the organotin compound is a dialkyltin dicarboxylate.

6. The sealant composition of any one of Claims 1 to 5 wherein the dialkyltin dicarboxylate corresponds to the formula $(R^2OC(O))_2\text{-}Sn\text{-}(R^3)_2$ wherein R^2 and R^3 are independently in each occurrence a C_{1-10} alkyl.

7. The sealant composition of any one of Claims 1 to 6 wherein the isocyanate content of the prepolymer is in the range of from 1.5 percent to 5.0 percent.

8. The sealant according to any one of Claims 1 to 7 wherein the organometallic compound is 1,1-dimethyltin dilaurate, 1,1-dibutyltin diacetate, 1,1-dimethyl dimaleate or a dialkyltin dimercaptide.

9. A method for bonding glass to a substrate which comprises contacting a sealant according to any one of Claims 1 to 8 with glass and another substrate with the sealant disposed between the glass and substrate and thereafter allowing the sealant to cure so as to bind the glass to the substrate.

10. A method according to Claim 9 wherein the substrate is metal, plastic or a composite which is coated with an acid resistant paint.

INTERNATIONAL SEARCH REPORT

Internatio   \pplication No
PCT/US 97/23370

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/10 C08G18/16 C08G18/18 C08G18/20 C08G18/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 533 275 A (ENICHEM SYNTHESIS S.P.A.) 24 March 1993 see claim 13; examples 18-25 ---	1,2,5,6
A	US 5 342 867 A (G.R.RYAN ET AL.) 30 August 1994 see column 5, line 52 - line 59 see column 1, line 4 - line 9; example 7 ---	1,2,5-10
A	EP 0 656 383 A (OSI SPECIALTIES LTD.) 7 June 1995 see claims 1-3,5,6 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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2

Date of the actual completion of the international search	Date of mailing of the international search report
28 April 1998	14 05 1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Angiolini, D